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A STABLE RADICAL COMPLEX OF PHTHALOCYANINE; GREEN

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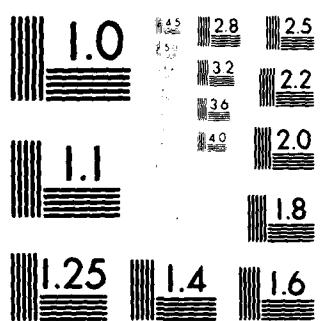
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A Stable Radical Complex of Phthalocyanine:  
Green Bisphthalocyaninatoneodymium(III)

by

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ABSTRACT:

A stable-neutral radical complex of bisphthalocyaninatoneodymium(III) was prepared by a facile method. The radical is evident from EPR and magnetic susceptibility.

A Stable Radical Complex of Phthalocyanine: Green Bisphthalocyaninatoneodymium(III)

Sir:

Stable radicals such as triphenylmethyl, DPPH, and diethylnitroxide are known to have wide applications as standard samples for EPR measurements, radical capture experiments, and spin labeling techniques.<sup>1</sup> Recently, stable radical species of 3d-metallocphthalocyanines have become important for their similar structure with metalloporphyrins of which radicals play a dominant role in biological electron transfer.<sup>2</sup> However, the synthesis of their radicals have some difficulties and the radicals sometimes contain impurities.<sup>3</sup> We wish to report here that a neutral-stable radical of bisphthalocyaninatoneodymium(III) was generated by a facile reaction and was evident from EPR and magnetic susceptibility. The green radical was generated as a monosolvated species of dichloromethane by refluxing a blue bisphthalocyaninatoneodymium(III) complex in dichloromethane for a few hours. Anal. Calcd for C<sub>64</sub>H<sub>32</sub>N<sub>16</sub> Nd · CH<sub>2</sub>Cl<sub>2</sub>: Cl, 5.66%, Found: Cl; 5.71%. Mass: m/e 88(CH<sub>2</sub>Cl<sub>2</sub><sup>37</sup>, 11%), 86(CH<sub>2</sub>Cl<sup>37</sup>Cl<sup>35</sup>, 67%), and 84(CH<sub>2</sub>Cl<sub>2</sub><sup>35</sup>, 100%).<sup>4</sup> The molecular structure of the green compound was reported in a previous paper; a neodymium(III) ion occupies a central position between two parallel, but staggered phthalocyanine ligands.<sup>5</sup> The synthesis of the blue compound has been described previously.<sup>6</sup> In the EPR spectra of the blue and green species in the polycrystalline state, the latter exhibited a strong EPR signal ( $g = 2.0029$ ), while the former did not show any EPR signal. The green compound diluted with the blue showed anisotropy ( $g_1 = 2.001$ ,  $g_2 = 2.004$ ) (Fig. 1).<sup>7</sup>

Figure 1

No hyperfine structure of these signals was obtained in the solid (also in a dichloromethane solution) either at room temperature or at liquid nitrogen temperature, consistent with the case of a molecular complex of bisphthalocyaninatoeuropium(III) with iodine.<sup>8</sup> The spectrum is also the same with that of the organic-free radical observed in the study of an electrochemical redox of lutetium phthalocyanine.<sup>9</sup> When the mixed solution of tetrahydrofuran and a small amount of dichloromethane containing the blue compound was irradiated by an ultraviolet light for several minutes, the color of the solutions changed from blue to green, while it did not change in the dark (Fig. 2).<sup>10</sup>

Figure 2

An infrared study of the blue and green compounds showed that imine hydrogen of the phthalocyanine ligand of the blue compound is not present in the green.<sup>11</sup> These results suggest a photo-induced oxidation of the blue compound. That is, imine hydrogen of the blue compound is abstracted by a small amount of photo-induced  $\text{CH}_2\text{Cl}\cdot$  or  $\text{Cl}\cdot$  radical: initially, a  $\sigma$ -radical may be generated and subsequently turns to a stable  $\pi$ -radical. Magnetic susceptibility measurements of these compounds showed that the blue complex has three unpaired electrons  $\mu_{\text{obs}} = 3.44$  B.M. at room temperature,  $\mu_{\text{cal}} = 3.62$  B.M. for the neodymium(III) ion, while the green has four unpaired electrons (4.24 B.M. at room temperature,  $\mu_{\text{cal}} = 3.62 + 1.73 = 5.35$  B.M.).<sup>12</sup> The magnetic susceptibility of the green complex showed a magnetic field dependence, while that of the blue was not dependent on the magnetic field. Furthermore, the effective magnetic

moment of the green decreased with decreasing temperature (3.65 B.M. at 73°K), but that of the blue did not change significantly with decreasing temperature. These magnetic results demonstrate that the green compound contains one organic-free radical, which could have an exchange interaction with the f-electrons of the central neodymium(III) ion as is found in some radicals of 3d-transition metal complexes of phthalocyanine.<sup>3</sup>

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4. The mass spectrum was measured in the temperature of 300-340°C to identify existence of dichloromethane in the compound. At this temperature, bisphthalocyanatoneodymium(III) did not sublime.
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12. Susceptibility measurements were made with a Faraday method with mercury tetrathiocyanatocobaltate for calibration. Diamagnetic corrections were estimated from the diamagnetism of metal-free phthalocyanine, but were comparatively small.

### Figure Captions

**Figure 1.** X-band EPR signals of the green bisphthalocyaninatoneo-dymium(III) complex in the solid state at 77°K. The line 2 respects the signal of the green compound diluted by the blue (1:100). Gains are  $8.0 \times 10^1$  and  $2.0 \times 10^4$  for the line (1) and the line (2), respectively.

**Figure 2.** UV light effects on conversion of the blue compound to the green in the tetrahydrofuran solution containing a small amount of dichloromethane. 1) Before irradiation, 2) 2 minutes after irradiation, 3) 4 minutes, 4) 6 minutes, 5) 8 minutes, 6) 10 minutes.

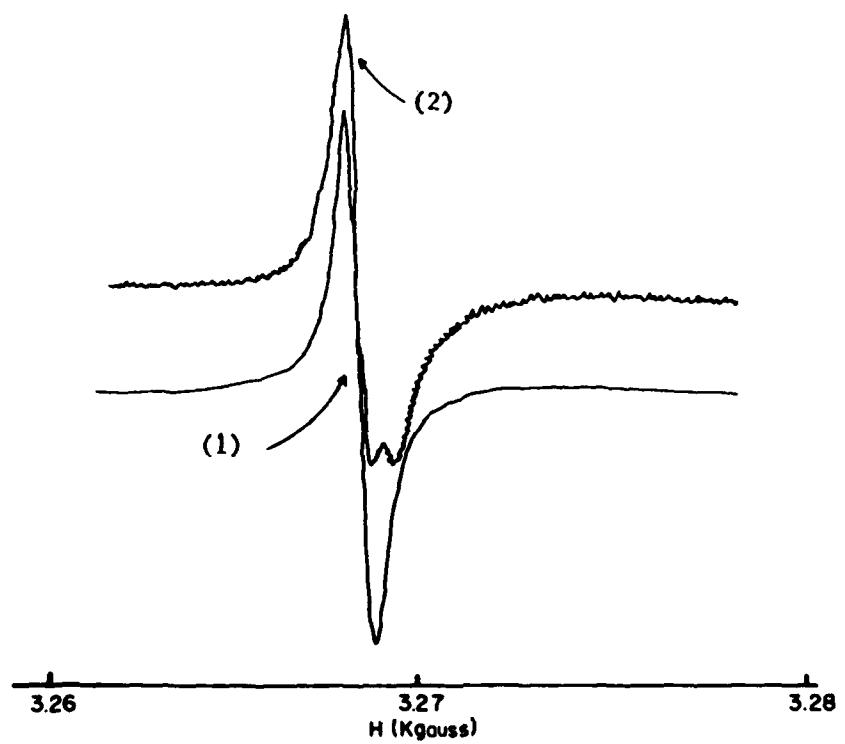


Figure 1, Tsutsui

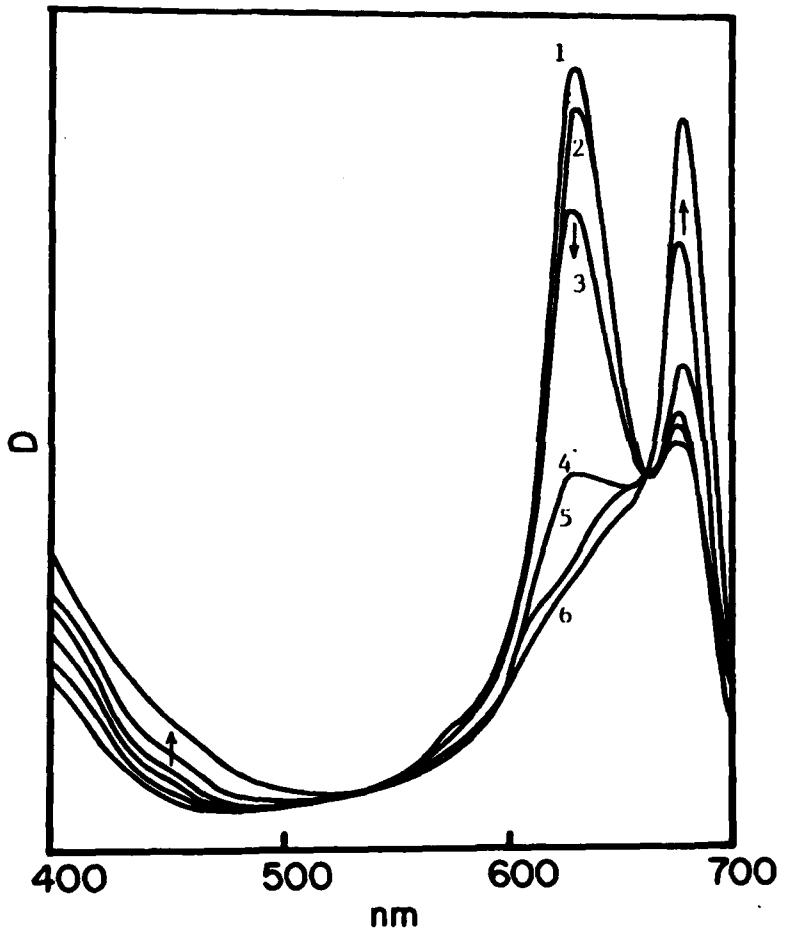


Figure 2, Tsutsui

